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Title:

Large-volume ultrafiltration for the study of radiocarbon signatures and size vs. age relationships in marine dissolved organic matter

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Abstract

In recent decades, tangential-flow ultrafiltration (UF) technology has become a primary tool for isolating large amounts of “ultrafiltered” marine dissolved organic carbon (UDOC; 0.1 μm to ~ 1 nm) for the detailed characterization of DOC chemical composition and radiocarbon ($\delta^{14}\text{C}$) signatures. However, while total DOC $\delta^{14}\text{C}$ values are generally thought to be quite similar in the world ocean, previous studies have reported widely different $\delta^{14}\text{C}$ values for UDOC, even from very similar ocean regions, raising questions about the relative “reactivity” of high molecular weight (HMW) DOC. Specifically, to what degree do variations in DOM molecular weight (MW) vs. composition alter its relative persistence, and therefore HMW DOC $\delta^{14}\text{C}$ values?

In this study we evaluate the effects of varying proportions of HMW vs. low molecular weight (LMW) DOC on UDOC $\delta^{14}\text{C}$ values. Using concentration factor (CF) as a proxy for MW distributions, we modeled the retention of both OC and $\delta^{14}\text{C}$ in several very large CF experiments (CF >3000), from three depths (20 m, 670 m, 915 m) in the North Pacific Subtropical Gyre (NPSG). The resulting DOC and $\delta^{14}\text{C}$ UF permeation coefficients generally increase with depth, consistent with mass balance trends, indicating very significant permeation of LMW, ^{14}C -depleted DOC at depth, and higher recoveries of $\delta^{14}\text{C}$ -enriched, HMW DOC in the surface. In addition, changes in CF during sample concentration and ionic strength during sample diafiltration had very large and predictable impacts on UDOC $\delta^{14}\text{C}$ values.

Together these results suggest that previously reported disparities in UDOC $\delta^{14}\text{C}$ values are reconciled by linked trends of $\delta^{14}\text{C}$ content vs. MW. At low CFs, UDOC samples have similar $\delta^{14}\text{C}$ values to total DOC. In contrast, UDOC samples collected at extremely high CFs (and after diafiltration) have more positive $\delta^{14}\text{C}$ values. We demonstrate that the observed relationships between UDOC $\delta^{14}\text{C}$ and CF derived from our data can directly explain offsets in all previously published UDOC $\delta^{14}\text{C}$ values for the NPSG. While CF is not traditionally considered in UF studies, our results indicate it can substantially influence the interpretation of UDOC ^{14}C “age,” and thus reactivity, in the marine environment. In addition, our results indicate that CF can be in fact be used as a proxy for average MW. We suggest that a targeted-CF-UF approach, coupled with molecular-level $\delta^{14}\text{C}$ analyses, presents a new approach to studying relationships between molecular size, age, and “labile” DOC distributions in the ocean.

1. Introduction

At ~662 Pg C (Hansell et al., 2009), oceanic dissolved organic matter (DOM) represents one of the largest active pools of reduced carbon on Earth (Hedges, 1992), and the linkages between DOM production and remineralization are of primary importance to the ocean carbon cycle. Perhaps one of the most influential observations shaping our understanding of marine DOM cycling and reactivity has been the global distributions of dissolved organic carbon (DOC) and its radiocarbon ($\delta^{14}\text{C}$) value (Druffel et al., 1992; Williams and Druffel, 1987). The strong ^{14}C -depletion of deep ocean DOC with respect to dissolved inorganic carbon (DIC; by ~300‰) suggests that DOM in the deep ocean (at ~6,000 ^{14}C ybp) is highly resistant to degradation and persists over multiple ocean mixing cycles. However, the low concentration of DOC relative to abundant seawater salts (~1 mg l^{-1} DOC to ~35,000 mg l^{-1} salt) has made more detailed molecular level and isotopic DOM analyses difficult. As a consequence, the role of specific DOM constituents, that combine to form these bulk ^{14}C “ages”, and their individual cycling rates remain poorly understood.

In recent years, the application of tangential-flow ultrafiltration (UF) to the marine DOM pool has provided a highly effective tool for the chemical and isotopic characterization of marine DOM (Aluwihare et al., 2002; Benner et al., 1992; McCarthy et al., 1996), in particular the most reactive HMW components (Repeta et al., 2002). Together, the isolation of DOM collected by UF, coupled with $\delta^{14}\text{C}$ measurements and molecular analysis, have provided a powerful new approach for understanding sources and cycling rates of individual DOM constituents in the carbon cycle (Loh et al., 2006; Loh et al., 2004; Repeta and Aluwihare, 2006). Because large-volume UF uses an open, continually recycling system (through which essentially unlimited seawater volumes can be processed), it allows for the isolation of >1 gram of DOC. Typically,

sample concentration is followed by diafiltration to remove sea salts. DOM isolated by UF represents organic material that passes through a 0.1 – 0.2 μm filter (to remove most particles and prokaryotic organisms) but is retained by a ~ 1 nm (1,000 Dalton) nominal molecular weight cut-off (NMWCO) membrane. Some studies refer to material isolated by UF as “colloidal” based on this nominal size range (Buesseler et al., 1996; Dai et al., 1998; Guo and Santschi, 1996; Guo et al., 2000). However, work focused on the oceanic DOM pool has usually used *ultrafiltered* DOM (UDOM), a designation that makes no assumptions about its physiochemical form in the ocean. This definition also reflects the fact that while the isolated material is of higher average molecular size than total DOC, many bulk and compositional properties of UDOM (e.g. C/N_a ratio and $\delta^{13}\text{C}$ composition) are generally similar to the total DOC pool (Amon and Benner, 1994, 1996; Benner et al., 1997; Benner et al., 1992; Loh et al., 2004; McCarthy et al., 1996; McCarthy et al., 1997).

In contrast, the radiocarbon isotopic ($\Delta^{14}\text{C}$) value of UDOM is one bulk compositional property that differs from total DOC. Published $\Delta^{14}\text{C}$ signatures of UDOM are generally more positive than total DOC $\Delta^{14}\text{C}$ (McNichol and Aluwihare, 2007). This is consistent with the idea that HMW DOM predominately represents the “semi-reactive” component of ocean DOM (Amon and Benner, 1994; Benner et al., 1992). Understanding the turnover of this pool is critical because this material advects carbon to the sub-surface ocean, thereby closing key carbon budgets (Hansell et al., 2002). However, previous studies have also reported widely different $\Delta^{14}\text{C}$ values for UDOM from identical ocean regions. For example, previously reported $\Delta^{14}\text{C}$ values from contemporaneous UDOM isolations taken at the same location in the North Pacific Subtropical Gyre (NPSG), using the same membrane pore sizes, differ by $\sim 130\%$ (Loh et al., 2004 $\Delta^{14}\text{C} = -92 \text{ ‰}$; Repeta and Aluwihare, 2006 $\Delta^{14}\text{C} = +42 \text{ ‰}$). Even larger disparities (~ 240

1 ‰) have been reported from deep ocean UDOM samples, again with identical membrane pore
2 sizes, taken at the same location and depth (670m: Guo and Santschi, 1996 $\delta^{14}\text{C} = -502$ ‰;
3 Repeta and Aluwihare, 2006 $\delta^{14}\text{C} = -262$ ‰). Because UDOM $\delta^{14}\text{C}$ values are often used to
4 interpret “labile” and HMW DOC reactivity in the marine environment, these offsets in UDOM
5 $\delta^{14}\text{C}$ signatures suggest very significant temporal vs. spatial variability in semi-labile DOM
6 formation processes and reactivity, even in similar ocean regions.

7 However, one alternate possibility is that variability in the distribution of sample molecular
8 weight (MW) in recovered UDOM might alter measured $\delta^{14}\text{C}$ UDOM values. Because UF
9 represents a progressive “distillation” of a complex molecular mixture (based primarily on
10 retention at a specified nominal MW cutoff), the molecular weight distribution within a specific
11 UDOM sample might significantly affect its measured $\delta^{14}\text{C}$ value. However, to date this has
12 never been directly evaluated; the majority of studies investigating UF as a tool for isolating
13 marine DOM have focused on establishing: 1) preliminary estimates of the molecular size
14 distributions of marine DOM (Sharp, 1973), 2) rigorous cleaning, and operating procedures for
15 evaluating the effects of membrane pore-size/manufacturer on the retention characteristics of
16 UDOM (Buesseler et al., 1996; Chin et al., 1998; Dai et al., 1998; Guo and Santschi, 1996;
17 Gustafsson et al., 1996), 3) the retention of trace metals complexed to DOM (Buffle et al.,
18 1992a; Guo et al., 2000) and 4) evaluating the chemical and stable isotopic composition of
19 UDOM (Benner et al., 1997). While these studies have provided invaluable guidelines for the
20 collection of UDOC, most have used relatively low concentration factors of < 100 ($\text{CF} = \text{sample}$
21 volume/retentate volume), and also relatively small sample volumes (200 l or less). In contrast,
22 recent interest in understanding individual DOM component cycling rates via $\delta^{14}\text{C}$
23 measurements (Loh et al., 2006; Loh et al., 2004; Repeta and Aluwihare, 2006) requires that

much larger sample volumes be processed to isolate sufficient material. However, no prior study has evaluated the recovery characteristics of DOM $\delta^{14}\text{C}$ during UF, or how UF processing might alter the $\delta^{14}\text{C}$ signature of isolated DOM, relative to that of the total DOM pool.

In this study, we model $\delta^{14}\text{C}$ and DOC measurements from a series of UF experiments taken from three depths (surface, and mesopelagic) in the NPSG, sampled from the Natural Energy Laboratory of Hawaii Authority (NELHA) site. In addition, we specifically examine how $\delta^{14}\text{C}$ values for UDOM are influenced by varying CF and diafiltration. We show that both CF and diafiltration, by creating widely different effective MW distributions, have profound, yet predictable effects on the $\delta^{14}\text{C}$ signature of UDOM (consistent with significant permeation of low molecular weight DOM). These models also reconcile $\delta^{14}\text{C}$ offsets reported in all previously published UDOM samples in the Pacific Ocean, with important implications for relative reactivity of the ocean's semi-labile DOM pool.

2. Methods

2.1 Study Site and Sample Collection

Seawater samples were collected in December 2005 from 20 m, 670 m, and 915 m intake pipes at the Natural Energy Laboratory of Hawaii Authority (NELHA); located on the big island of Hawai'i just north of Kailua-Kona (19°69'N, 156°03'W). The station is located on a steep marine volcanic escarpment on the "desert" side of the big island of Hawai'i, and has no terrestrial freshwater sources. At NELHA, large diameter pipes bring seawater to the surface at very high flow rates (36,000 - 50,000 l min⁻¹). Results from previous studies suggest that particulate organic matter (POM) and DOM isolated from NELHA are similar to samples from the HOT-ALOHA site and representative of the NPSG (Ingalls et al., 2006; Repeta and Aluwihare, 2006; Roland et al., 2009).

Sample water from surface and mesopelagic depths were first pre-filtered through a 50 μm plankton net in order to remove larger marine particles, and subsequently through pre-cleaned (10% HCl) Whatman[®] 0.2 μm Polycap[™] 75 TC polyethersulfone cartridge filters. Total dissolved organic matter samples (TDOC; $<0.2 \mu\text{m}$) were collected in precombusted (450°C , 5 hours) 2 L glass jugs with PTFE lined caps and were immediately frozen and stored until $\Delta^{14}\text{C}$ analysis at UCI. UDOM samples ($<0.2 \mu\text{m}$ to $\sim 1 \text{ nm}$) were obtained using two home-built UF systems. The structural system components, pumps, automation and plumbing used were analogous to those recently described by Roland et al., 2009. Prior to each use, UF membranes were rigorously cleaned using a series of detergent (0.01% Fisher FL-70), 0.01N HCl, 0.01N NaOH and were then rinsed thoroughly with > 40 liters of 18.2 M Ω Milli-Q water. Sub-sampling of the UDOM retentate along with measurements of permeate flow rates were used to monitor DOC mass balance. UDOM fraction recoveries were calculated using subsamples' DOC concentrations and sample volumes during each stage in the filtration (Table 1).

Briefly, the first “main filtration” system contained two large polyethersulfone (PES) UF membranes (GE Osmonics: GH 4040-C1072, NMWCO = 2.5 kDa) and a 100 L high-density polyethylene (HDPE) sample reservoir was used for the main sample concentration where sample feed solutions were continuously processed until a final sample throughput volume of $\sim 5,000 - 6,000 \text{ l}$ was obtained. Next, the sample feed was shut off and the remaining sample retentate was allowed to reduce from $\sim 100 \text{ L}$ to $\sim 20 \text{ L}$ and was then collected and transferred to a second UF system for further sample reduction and diafiltration. This second “reduction/diafiltration” system contained a single, smaller PES UF membrane (GE Osmonics: GE 2540-F1072, NMWCO = 1 kDa) and 4 l glass funnel sample reservoir. The 20 L sample was further reduced to $\sim 2 \text{ L}$ prior to diafiltration. For the purposes of modeling UF behavior in the

concentration mode later in the discussion, we make no distinction between these first filtration steps, and consider all sample concentration (i.e. 5,000 L to ~2 L) to represent the UF “concentration mode”. Salty 2 L retentates were immediately frozen and later diafiltered in the laboratory at University of California, Santa Cruz. In order to conserve sample for future analysis, only ~200 ml splits of this salty 2 L retentate were diafiltered. Diafiltration of the salty UDOM 200 ml retentate splits was performed by bringing sample volumes up to ~2 L with 18.2 M Ω Milli-Q water and then gradually adding 20 L of Milli-Q water to the sample retentate at the same rate of fluid permeating the membrane (i.e. constant retentate volume). Final ~2 L diafiltered UDOM retentates were dried via centrifugal evaporation, homogenized with a mortar and pestle and subsequently stored in a desiccator cabinet in pre-combusted glass vials (450°C, 5 hours) prior to analyses.

In order to evaluate the permeation behavior of DOC and $\delta^{14}\text{C}$ during UF, several discrete DOC retentate sub-fractions were collected throughout each UF experiment (following methods set forth by Kilduff and Weber, 1992). Each ultrafiltered UDOC fraction was collected at a defined CF, or in the case of the final UDOC isolate, after diafiltration. For clarity, a summary of UDOC sub-samples is provided in Figure 1 (see *section 3.3* and *3.4* for a more detailed discussion of concentration vs. diafiltration UF modes). UDOC retentates were first sub-sampled from the main 100 L filtration system tank at a low CF (UDOC_{LCF}; sampled at CF ~30 - 40, corresponding to ~3,000 L total sample throughput) and were immediately stored frozen in the field. UDOC retentate sub-samples were also taken after ~4,000 – 6,000 L sample throughput at the end of the concentration mode (UDOC_{HCF}; CF ~3,000). Finally, we define the aforementioned final diafiltered UDOC retentate splits as “D-UDOC_{HCF}”.

2.2 Sample Preparations and Isotopic Analysis

Total DOC (TDOC), UDOC_{LCF} , UDOC_{HCF} , and D- UDOC_{HCF} concentrations ($\pm 1 \mu\text{M}$) were determined via high temperature combustion using a Shimadzu TOC-V at the University of California, Santa Barbara (UCSB Carlson Lab), and also based on manometric measurements during offline combustion for isotopic analyses. TDOC concentrations reported in this study represent the average of all values determined by both UV oxidation/vacuum line purification at UC Irvine following the methods of Beaupré et al., (2007) and those determined by high temperature combustion at UCSB. Percent recoveries for each UDOC fraction are reported relative to TDOC concentrations (μM) and volume processed.

Natural abundance radiocarbon ($\Delta^{14}\text{C}$) determinations of all UDOC fractions were performed either at LLNL/CAMS or UC Irvine Keck Carbon Cycle AMS Laboratory following standard graphitization procedures (Santos et al., 2007; Vogel et al., 1987). Age-corrected $\Delta^{14}\text{C}$ values (‰) have been corrected for sampling year and year of analysis and are reported in accordance with conventions set forth by Stuiver and Polach (Stuiver, 1977) using the Libby half-life of 5,568 years. Reported values are given after subtracting sample preparation backgrounds based on a ^{14}C -free calcite standard and have been corrected for isotopic fractionation of $\delta^{13}\text{C}$. Isotopic results are reported as Fraction Modern (FM), $\Delta^{14}\text{C}$, $\delta^{13}\text{C}$, and conventional radiocarbon age (ybp). For TDOC and UDOC_{LCF} splits, $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ were measured after UV-oxidation and vacuum line extraction following established protocols at UCI (Beaupré et al., 2007). UDOC_{HCF} and D- UDOC_{HCF} $\Delta^{14}\text{C}$ measurements were performed via closed tube combustion and graphitization at LLNL/CAMS. Because UDOC_{HCF} fractions are inherently salty, 2.0 ml were pipetted into either precombusted quartz tubes for $\Delta^{14}\text{C}$ analyses, or to silver boats for CHN ($\delta^{13}\text{C}$) analyses. All UDOC_{HCF} samples were acidified (0.5 N HCl) and dried prior to these analyses; for CHN analyses, UDOC_{HCF} samples were oven-dried at 40°C ;

CHN splits, for $\Delta^{14}\text{C}$ analyses of UDOC_{HCF} samples were dried by lyophilization. UDOC_{HCF} and $\text{D-UDOC}_{\text{HCF}}$ $\delta^{13}\text{C}$ values were determined by CHN analysis at the University of California, Santa Cruz - Stable Isotope Laboratory using a Carlo Erba CHNO-S EA-1108 Elemental Analyzer and Thermo-Finnigan Delta Plus XP isotope ratio mass spectrometer. Results are reported in standard per mil (‰) notation and relative to V-PDB; $\delta^{13}\text{C}$ values have an overall analytical error of $\pm 0.1\%$. Reported LMW DOM % recovery, $\delta^{13}\text{C}$, and $\Delta^{14}\text{C}$ values for all UDOC fractions were determined via isotopic mass balance where $\Delta^{14}\text{C}_{\text{LMW}} = [(\text{TDOC})(\Delta^{14}\text{C}_{\text{TDOC}}) - (\text{DOC}_{\text{HMW}})(\Delta^{14}\text{C}_{\text{HMW}})]/(\text{DOC}_{\text{LMW}})$. Radiocarbon ages (ybp) are calculated using the relationship: ^{14}C ages (ybp) = $-8033 \cdot \ln(\text{Fm})$.

2.3 Permeation Models and Coefficients

We applied solute permeation models to the DOC and $\Delta^{14}\text{C}$ data presented in this study to examine the behavior of UF on the retention of DOC and $\Delta^{14}\text{C}$ -content at extremely high CFs. Models used in this study are identical to those described by Kilduff and Weber (1992). Briefly, solute retention behavior during UF is generally characterized by the extent of solute “rejection” (R) by the membrane, which is defined as:

$$R = 1 - C_p/C_f \quad (1)$$

Where C_p is the solute concentration in the sample permeate (LMW DOC), and C_f is the “feed” solute concentration in the sample retentate (both HMW and LMW DOC). This relationship can also be expressed in terms of the solute’s ability to permeate the UF membrane, or permeation coefficient (P_c). The P_c value of a given solution is related to membrane rejection factor in the concentration mode through the following relationship:

$$P_c = (1-R) \quad (2)$$

During UF in the “sample concentration mode”, the feed concentration of DOC ($C_{f\text{DOC}}$) is related to the concentration factor (CF) through the following relationship:

$$C_{f\text{DOC}} = C_{f0\text{DOC}} (\text{CF})^{(1-P_c)} \quad (3)$$

Where $C_{f0\text{DOC}}$ is the initial feed concentration (Total DOC), P_c is the permeation coefficient and $C_{f\text{DOC}}$ is the sample retentate concentration (UDOC). Following Kilduff and Weber (1992) and equation 3, in the concentration mode a log-linearized plot of $\ln (C_{f\text{DOC}}/C_{f0\text{DOC}})$ vs. $\ln (\text{CF})$ throughout a UF experiment in the concentration mode will yield a slope (m) = $1-P_c$, as indicated by the following expression:

$$\ln (C_{f\text{DOC}}/C_{f0\text{DOC}}) = (1-P_c) \ln (\text{CF}) \quad (4)$$

Kilduff and Weber (1992) also demonstrated that a log-linearized plot of $\ln (C_f)$ vs. $\ln (\text{CF})$ during the concentration mode yields a y-intercept equal to $C_{f0\text{DOC}}$. In this study and that of Kilduff and Weber (1992), $C_{f0\text{DOC}}$ is defined as the sample “feed” concentration at time = 0. In other words, $C_{f0\text{DOC}}$ is the DOC concentration of the sample fluid in the retentate reservoir just after it is filled (before any ultrafiltration takes place). Therefore, for the purposes of this study $C_{f0\text{DOC}}$ is considered equivalent to Total DOC. It is important to note that our definition of $C_{f0\text{DOC}}$ differs from that of Guo and Santschi (1996), where they measure the UDOC permeate (as opposed to retentate) fraction. Thus, in Guo and Santschi (1996), $C_{f0\text{DOC}}$ is not equivalent to Total DOC, but rather the initial concentration of LMW DOC in the sample fluid.

In this study, we use the same regression approach to evaluate the permeation behavior of DOC $\Delta^{14}\text{C}$ -content during our UF experiments for the following reasons: 1) to evaluate whether or not DOC $\Delta^{14}\text{C}$ -content permeates a UF membrane ideally with respect to permeation theory and 2) if so, to evaluate if this approach can reconcile the large offsets in previously reported UDOC $\Delta^{14}\text{C}$ signatures. If DOC $\Delta^{14}\text{C}$ -content permeates a UF membrane ideally as a function of CF, a

log-linearized plot of $\ln \Delta^{14}\text{C} (C_f/C_{f0})$ vs. $\log (CF)$ will demonstrate a statistically robust correlation and yield a slope $(m) = 1 - P_c$. Similarly, a log-linearized plot of $\ln \Delta^{14}\text{C} (C_f)$ vs. $\ln (CF)$ will yield a y-intercept of $\ln C_{f0 \ 14C}$ (or the $\Delta^{14}\text{C}$ signature of Total DOC). It is important to note that because “instantaneous” P_c values (i.e. derived directly from equations 1 and 2 at time $= t$) change significantly throughout UF, here we report “time/volume-integrated” P_c values (in accordance with Kilduff and Weber, 1992). These P_c values more accurately characterized the permeation behavior of the sample fluid over the entire experiment and are derived from the slopes of linear regression analyses described above. For our samples, we define DOC permeation coefficients as “ $P_{c \text{ DOC}}$ ” and $\Delta^{14}\text{C}$ permeation coefficients as “ $P_{c \ 14C}$ ”. Finally, a similar approach can be used to determine permeation behaviors during the diafiltration mode. In this case, as defined by Kilduff and Weber (1992), a plot of $\log (C_f/C_{f0})$ vs. (V_p/V_0) will yield a slope (m) of $-P_c$. Where C_{f0} is the initial retentate concentration before starting diafiltration, V_0 is the system volume and V_p is the permeate volume.

2.4 Terminology and Conventions for Modeling DOC Molecular Weight Fractions

As described above, our data represent discrete sub-samples taken from the retentate solution throughout several UF experiments (Figure 1). These represent a continuum in the mixture of both high molecular weight (HMW, defined as material rejected by a membrane, nominally $>1,000$ Dalton) and low molecular weight (LMW; defined as material which can pass membrane, nominally $<1,000$ Dalton) DOM. In the following discussion, we refer to all of our retentate sub-samples as “ultrafiltered” DOC (UDOC). We also use the terms LMW and HMW as operational definitions based solely on membrane rejection. It is also possible to model DOM constituents of additional molecular weight categories (e.g. LMW, “intermediate” MW and HMW; Benner et al., 1997). However, while it may be true that individual components of

“intermediate” molecular weight may permeate the system at different rates vs. “true” LMW material (e.g. Guo et al., 1996; Benner et al., 1997), if there is no HMW membrane breakthrough, then ultimately a DOC mixture is defined by the mixture of these two basic operational components. This is particularly true in high CF experiments. Using only the HMW vs. LMW division thus provides an accurate, and also simplified, framework to interpret UF retention and permeation behavior.

3. Results and Discussion

3.1 Recovery of Ultrafiltered DOC

In the surface, UDOC fractions had overall higher recoveries at each stage in filtration than deep UDOC fractions at comparable CFs (Table 1). There was a consistent relationship at each depth between DOC recovery and CF. UDOC collected at low CFs had higher overall recoveries of TDOC (CF <50; $UDOC_{LCF} = 32\%$ surface, 22% deep), and UDOC recoveries at high CFs had lower overall recoveries of TDOC (CF ~3,000; $UDOC_{HCF} = 21\%$ surface, 11-12% deep). Diafiltration also substantially decreased TDOC recoveries ($D-UDOC_{HCF} = 13\%$ surface, 7-8% deep; Table 1). UDOC sub-sample recoveries at low CFs indicate that initial permeation of DOC is significant, with approximately 68% and 78% permeation of DOC at CF < 50 for surface vs. deep, respectively. For the concentration mode, mass balance recoveries indicate that the permeation of “LMW” DOC accounts for 79% of TDOC in the surface and ~89% of TDOC at depth. Final DOC recoveries ($D-UDOC_{HCF}$) are slightly lower than recent work using UF membranes of similar NMWCO, but different manufacturer (Aluwihare et al., 2002; Benner et al., 1997; Loh et al., 2004; Santschi et al., 1995).

1 A dramatic increase in measured retentate DOC concentration is observed with increased
2 CF at all depths (Figure 2A). However, when normalized to TDOC and volume filtered, a
3 progressively smaller fraction of the TDOC pool is in fact retained as the experiment progresses
4 (Table 1). Put another way, continuing DOC loss is observed from the system during both
5 sample concentration and diafiltration, but the *relative percentage* of DOC loss progressively
6 decreases. For example, in the surface we observed a 68% decrease in total recovery from TDOC
7 to UDOC_{LCF} and subsequently smaller decreases in total recovery between UDOC_{LCF} and
8 UDOC_{HCF} (11%).

9 During the diafiltration mode we observe large decreases in retentate DOC concentration
10 for all depths. The proportional diafiltration losses are much greater in the surface, vs.
11 mesopelagic (Figure 2A). At 20 m, diafiltration resulted in an additional 50% loss of the retained
12 UDOC_{HCF} (i.e., 43.2 mM of UDOC_{HCF} dropped to 22.5 mM D- UDOC_{HCF} , after diafiltration;
13 Table 1). At the 670 m and 915 m depths, analogous losses were much lower and nearly equal
14 ($28.5\% \pm 0.3\%$, $n = 2$). These values are consistent with previous observations of DOC loss
15 during sample diafiltration (Benner et al., 1997; Guo and Santschi, 1996; Guo et al., 2000),
16 however, because we did not perform detailed sampling during the diafiltration mode, we do not
17 further discuss the permeation behavior of DOC during diafiltration in this study. However, this
18 comparison does illustrate that for very large volume filtrations, CF has a larger cumulative
19 effect on mass retention than does diafiltration.

20 The overall observation of DOC loss with increasing CF is consistent with previously
21 reported permeation behaviors for seawater DOM, however an important difference is that our
22 data indicate that much higher CFs are required to fully remove LMW material. Previous work
23 has shown that at lower CFs ($\sim 20 - 100$), HMW DOC concentrations can be overestimated by up

1 to ~30% due to retention of LMW DOM (Guo and Santschi, 1996). Previous studies have also
2 indicated that using CFs as low as 40 are generally sufficient to remove LMW material, and
3 isolate a relatively “pure” HMW DOC sample (as defined by a membrane NMWCO, and
4 assuming no breakthrough or concentration polarization; Guo et al., 2000). While in our study
5 we observed no breakthrough of HMW DOC (*later discussed in section 3.2 and 3.3*), our results
6 indicate a large fraction of LMW DOC is retained at $CF < 40$. In addition, from $CF = \sim 40$ to
7 $\sim 3,000$ we observed additional loss of LMW material equivalent to 10 - 11% of the TDOC pool.
8 At $CF = 40$ in our experiments, apparent HMW DOC concentrations are overestimated by ~20%
9 vs. recoveries at $CF \sim 2,500$. These observations are consistent with other studies suggesting that
10 much larger CFs are needed to fully remove LMW material and isolate a “pure” HMW sample.
11 For example, Benner et al. (1997) found through modeling a mixture of LMW, “intermediate”
12 and HMW DOC components (each with its own P_c value), that $CF \sim 100$ removes 98% “LMW”
13 and 86% of “intermediate MW” material, and modeled HMW concentration in the UDOC
14 retentate for a large-volume isolation was greater than 95% (UDOC at $CF = 1,000$). Our
15 modeled results suggest that even after $CF \sim 2,500$ in the concentration mode, roughly 5-8%
16 LMW DOC remains in the UDOC retentate solution, which then permeates during diafiltration
17 ($UDOC_{HCF}$ to $D-UDOC_{HCF}$). Thus, while previously modeled results for $CF = 1,000$ are
18 consistent with our observations, the precise amount of LMW DOC remaining in the UDOC
19 solution during large-volume isolations is either 1) underestimated by these models or 2)
20 dependent on the specific environment in which samples are taken (e.g. the nature of the HMW
21 vs. LMW DOC mixture sampled). Later we invoke several permeation models to explain this
22 behavior in the concentration mode (*section 3.3 and 3.4*). Together, these data indicate that low
23 CFs are not adequate to fully remove LMW material (i.e. when UF is conducted at low CF, a

much more representative sample of total DOC is isolated due to both LMW and HMW retention).

3.2 Carbon Isotopic Composition

A summary of carbon isotope data is provided in Table 1. Stable carbon $\delta^{13}\text{C}$ values for TDOC and all UDOC fractions fall within typical ranges for DOM from the NPSG (-20 ‰ to -22 ‰) with the possible exception of TDOC from 915 m ($\delta^{13}\text{C} = -23.2$ ‰), which was slightly lower than typical TDOC $\delta^{13}\text{C}$ values from the Central North Pacific (CNP; Druffel et al., 1992). These TDOC $\Delta^{14}\text{C}$ values are the first reported TDOC $\Delta^{14}\text{C}$ measurements for all water source depths available at the NELHA site, and are $\Delta^{14}\text{C} = -246 \pm 5$ ‰, -479 ± 9 ‰ and -446 ± 8 ‰ for 20 m, 670 m and 915 m depths, respectively. These values are consistent with ship-based measurements from the CNP (Druffel et al., 1992), further confirming isotopic and molecular-level data which suggests DOM from NELHA samples is representative of this general ocean region (Ingalls et al., 2006; Repeta and Aluwihare, 2006).

Even though all $\Delta^{14}\text{C}$ values are in expected ranges, the 33‰ TDOC $\Delta^{14}\text{C}$ increase observed between 670 m and 915 m is the opposite of a typical depth profile. While it might be tempting to attribute this to a measurement error, we note a similar unexpected increase in $\Delta^{14}\text{C}$ values was observed in bacterial nucleic acids isolated from the same NELHA water sources (Hansman et al., 2009). In addition, the TDOC concentration at 915 m is slightly elevated vs. that at 670 m (43 vs. 40 μM) and its $\delta^{13}\text{C}$ value more negative than expected (-23.2‰). Together these observations would be consistent with an increase in DOC derived from surface-derived POC having nearly modern $\Delta^{14}\text{C}$ values. While we cannot fully explain these offsets from expected trends, it is important to emphasize that for the main purposes of this study they are inconsequential: i.e., water from 670 m and 915 m are both clearly oceanic “deep” water in terms

of their TDOC and $\delta^{14}\text{C}$ values, so to first order, these samples will represent independent replicates of oceanic deep water for our tests of UF behavior. However, as discussed below, for some of the modeling approaches the offsets between depths do alter resulting regressions and other finer scale results.

All UDOC sub-fractions had more positive $\delta^{14}\text{C}$ values with respect to TDOC, however, there was also a consistent trend of increasing $\delta^{14}\text{C}$ value with higher CFs. UDOC_{HCF} retentate subsamples were the most ^{14}C -enriched ($\text{UDOC}_{\text{HCF}} \delta^{14}\text{C} = -80\text{‰}$, -393‰ and -415‰), while UDOC_{LCF} retentate subsamples were less offset vs. TDOC at 20m and 670m ($\delta^{14}\text{C} = -131\text{‰}$ and -424‰ , respectively). The 915 m UDOC_{LCF} subsample was again slightly anomalous in terms of its UDOC_{LCF} fraction, being ^{14}C -depleted with respect to TDOC (-552‰ vs. -446‰ respectively). Results from an isotopic mass balance indicate this depleted UDOC_{LCF} value can be accounted for by a $\sim 34 \mu\text{M}$ loss of LMW DOC having a $\delta^{14}\text{C}$ signature slightly more positive with respect to TDOC (-416‰ vs. -446‰ respectively: Table 1). This explanation would be consistent with a slightly more positive $\delta^{14}\text{C}$ LMW contribution to the DOC pool from particle remineralization at this depth, perhaps from bottom accumulation of sinking material, or an intermediate nepheloid layer at this depth impinging on the steep volcanic escarpment near Keahole Point.

D- UDOC_{HCF} retentates had the most positive $\delta^{14}\text{C}$ values of all sampled UDOC sub-fractions. These D- UDOC_{HCF} values ($\delta^{14}\text{C} = -6\text{‰}$, -306‰ and -345‰ at 20 m, 670 m and 915 m depths, respectively) are in agreement with previously reported “high CF” UDOC $\delta^{14}\text{C}$ values from NELHA (Repeta and Aluwihare, 2006). The relative increase in $\delta^{14}\text{C}$ observed with diafiltration for each depth was very similar (Figure 2B; average $\delta^{14}\text{C}$ enrichment = $+77\text{‰} \pm 9\text{‰}$, $n = 3$). While this might initially suggest that similar LMW components are being

1 permeated during diafiltration at all depths, isotopic mass balance results indicate clear
2 differences between LMW material lost during diafiltration in the surface vs. mesopelagic. In the
3 surface, LMW DOC lost during diafiltration is only slightly more positive with respect to TDOC
4 (LMW $\delta^{14}\text{C} = -206\text{‰}$ vs. TDOC $\delta^{14}\text{C} = -246\text{‰}$), while at depth LMW material lost during
5 diafiltration has far more negative $\delta^{14}\text{C}$ values (LMW $\delta^{14}\text{C} = -519\text{‰}$ and -588‰ for 670 m and
6 915 m, respectively). This difference is also consistent with strong mass balance offsets between
7 surface and deep LMW $\delta^{14}\text{C}$ values determined for the entire UF experiment (i.e. material lost
8 from TDOC to D-UDOC_{HCF}; $\delta^{14}\text{C} = -281\text{‰}$ surface vs. n=2 average -473‰ at depth). While in
9 general these LMW DOC $\delta^{14}\text{C}$ values are consistent with previously determined values by
10 isotopic mass balance by Loh et al. (Loh et al., 2004), the large change in LMW $\delta^{14}\text{C}$ content
11 which occurs during UF presented in this study suggests that UF and diafiltration can have an
12 appreciable effect on resulting “HMW” $\delta^{14}\text{C}$ values.

14 3.3 DOC and Radiocarbon Permeation Models

15 In order to evaluate whether marine DOC retention at very high CF remains consistent
16 with the ideal UF theory, as is observed at low CF in previous work (Buesseler et al., 1996; Guo
17 and Santschi, 1996; Guo et al., 2000), we applied established UF permeation models to our
18 UDOC fractions. Similar models are typically used to evaluate the permeation/retention behavior
19 of organic macromolecules (Guo et al., 2000), and can be applied to both sample concentration
20 and diafiltration mode. If a given solute performs according to UF theory, the HMW component
21 will be rejected by the membrane at a constant rate throughout the experiment, no breakthrough
22 of HMW component will occur, and there will be no significant macromolecular accumulation
23 on the membrane surface (Buffle et al., 1992b). As described in the methods, under these
24 conditions, a log-log plot of mass vs. CF should yield a straight line, and the y-intercept should

correspond to the log of initial DOC concentration in the feed solution (i.e., UDOC at $\text{CF} = 1$, or $C_{f0 \text{ DOC}}$). Thus applying this approach in solutions containing a complex mixture of molecules, including oceanic DOC (Guo and Santschi, 1996; Guo et al., 2000), can be used to test these assumptions.

DOC permeation models demonstrate robust correlations for DOC at all depths, with R^2 values >0.98 (Figure 3A; Table 2A). The model-derived y-intercepts also closely match our measured TDOC values for the 20m and 670 m depths, estimates of $C_{f0 \text{ DOC}}$ fall within $\pm 2 \mu\text{M}$ of measured TDOC (Table 2), providing a robust verification of the application of UF models to these data. The 915 m $C_{f0 \text{ DOC}}$ value was lower than measured TDOC, yet is still within one standard deviation of the measured 915 m value ($C_{f0 \text{ DOC}} = 35 \pm 15 \mu\text{M}$ vs. $\text{TDOC} = 43 \pm 2 \mu\text{M}$). This is likely related to the unexpected higher TDOC concentration at this depth discussed earlier. However, we note that the model estimated value is actually closer to previously determined TDOC values from similar depths in the CNP ($38 \mu\text{M}$ at 900 m; Druffel et al., 1992), suggesting that UF permeation models based on multiple measurements can essentially “dilute” the effect of a single uncharacteristic value. This indicates that even at extremely high CFs, concentration polarization and HMW breakthrough for marine DOC are negligible, such that theoretical UF behavior is maintained. This also supports a simple division (in terms of membrane rejection behavior) between HMW and LMW pools in ocean DOM. In other words, since there is no significant breakthrough of *any* HMW component ($>1000 \text{ kDa}$) during even very high CF experiments, the HMW mixture ($>1000 \text{ kDa}$) within seawater DOC also behaves ideally. Overall, this implies that all changes in DOC permeation (and also associated $\Delta^{14}\text{C}$ value) can be ascribed to LMW DOC that is being retained at lower CF, rather than to selective breakthrough of some HMW components.

We also applied UF permeation models to our $\delta^{14}\text{C}$ data. To our knowledge, this is the first study to examine the effects of UF on the $\delta^{14}\text{C}$ content of DOC using this approach. As discussed in the methods, $\delta^{14}\text{C}$ permeation model results can be interpreted in a similar manner to DOC: using R^2 and intercept results to evaluate if there is a consistent relationship between retained $\delta^{14}\text{C}$ and HMW vs. LMW fractions. The regression results (Figure 3B) demonstrate that the $\delta^{14}\text{C}$ content of UDOC is also highly correlated to CF (Table 2B; $R^2 > 0.97$ for 20 m and 670 m). This is similar to DOC models, indicating that retention and permeation of DOM $\delta^{14}\text{C}$ -content during concentration mode also follows theoretical UF behavior. The log y-intercepts ($C_{f0\ 14C}$) for the 20 m and 670 m depths yield TDOC $\delta^{14}\text{C}$ values of $C_{f0\ 14C} = -232\text{‰}$ for 20 m and -474‰ for 670 m. As in the case for $C_{f0\ \text{DOC}}$, if UF behavior of $\delta^{14}\text{C}$ is ideal, then these values should match the $\delta^{14}\text{C}$ content of the feed solution at CF = 1 (TDOC). Our modeled $C_{f0\ 14C}$ values are in fact indistinguishable from our measured TDOC $\delta^{14}\text{C}$ values. However, again the results for 915 m are anomalous. The high p -value and lack of correlation (Table 2B) may be due to the lack of a significant slope ($m \sim 0.01$). However, despite the lack of significance and relatively large error (Table 2B), the 915 m modeled TDOC $\delta^{14}\text{C}$ value nevertheless falls very close to the measured TDOC $\delta^{14}\text{C}$ value ($C_{f0\ 14C} = -487\text{‰}$ vs. measured TDOC = -446‰). In addition, the intercept value is also very similar to the $\delta^{14}\text{C}$ signature reported for 900 m NCP (-470‰ , Druffel et al., 1992). Overall, despite the uncertainties at the 915 m depth, the data strongly indicates that $\delta^{14}\text{C}$ permeation models can be used to directly evaluate a relationship between CF and retentate $\delta^{14}\text{C}$ values at the surface and mesopelagic depths.

3.4 Permeation coefficients: an exploration of DOM molecular weight and $\delta^{14}\text{C}$ distribution

UF model-derived permeation coefficients (P_c) represent a ratio of solutes permeating a UF membrane (LMW) to those retained by the UF membrane (HMW), and can be calculated

1 either instantaneously or over the course of an entire UF experiment (see *methods*). Previous
2 work has shown that P_c and C_{f0} values determined by permeation models (analogous to this
3 study) can be used to more accurately determine both LMW solute permeation characteristics,
4 and also solute molecular size distributions in natural waters (Logan and Qing, 1990). Because
5 traditional DOC mass balance calculations inherently depend on running UF experiments to a
6 high CF to fully remove LMW material, at lower CFs these mass balances can be misleading by
7 underestimating the amount of LMW solutes that permeate the membrane. As a result (and as
8 our own data confirms), this approach can potentially greatly overestimate HMW recoveries. In
9 contrast, permeation models quantify membrane rejection and the initial concentration of the
10 feed solution (in our case TDOC) independent of sample volume filtered or CF. Thus, using P_c
11 values determined from DOC measurements during UF have the potential to be a more accurate
12 way to determine HMW vs. LMW abundance and molecular weight distributions of DOC within
13 natural waters.

14 To better illustrate the meaning of these coefficients, and the effect changing TDOC
15 molecular weight distributions can have on P_c values, a conceptual model summarizing both
16 theoretical limits and prior measured P_c values are presented in figure 4. The limits of P_c values
17 range from $P_{c\text{ DOC}} = 0$ to $P_{c\text{ DOC}} = 1.0$. If $P_{c\text{ DOC}} = 0$, and a slope of $m = 1$, there is 100% sample
18 retention, meaning that the TDOC mixture is comprised *only* of HMW DOC, and none of this
19 HMW DOC permeates the system. In contrast, if $P_{c\text{ DOC}} = 1.0$, there is 100% sample permeation
20 from the system, meaning that TDOC is comprised *only* of LMW DOM, which is significantly
21 smaller than the membrane NMWCO. Figure 4 also illustrates the influence of MW diversity on
22 P_c values, using three modeled DOC mixtures made from five molecular probes of varying MW
23 and membrane rejection properties (previously determined by Guo et al. 2000). These include:

1 10 kDa Dextran ($P_c = 0.0$), 3 kDa Dextran ($P_c = 0.03$), 1.33 kDa Vitamin B12 ($P_c = 0.15$), 0.612
2 kDa Glutathione ($P_c = 0.16$) and 0.495 kDa Rhodamine ($P_c = 0.60$). Line A in figure 4
3 represents an equal mixture of all five probes (20% each, resulting $P_c = 0.085$), whereas line B
4 (1% 10 kDa Dextran, 99% 0.495 kDa Rhodamine) and C (100% 0.495 kDa Rhodamine) are
5 mixtures dominated by LMW compounds. The TDOC solutions containing a higher abundance
6 of LMW molecules will have P_c approaching 1.0, whereas TDOC solutions rich in HMW
7 molecules will have lower P_c values, approaching zero. However, the additional influence of
8 mixtures is clear in the relative positions of line B and C: addition of only 1% of a higher MW
9 component causes a much larger logarithmic shift in P_c value (from Line C, $P_c = 0.60$ to Line B,
10 $P_c = 0.47$).

11 This example illustrates how the relative proportion of LMW permeation vs. HMW
12 retention can yield potentially more sensitive information regarding the general DOC MW
13 distribution in a solution. Using this conceptual framework, and assuming ideal UF behavior, the
14 proportion of HMW and LMW pools determined by UF permeation models may be more
15 accurate than traditional mass balance determinations, and thus have the potential to act as
16 proxies for relative changes in the molecular size distributions (LMW vs. HMW) of DOM at a
17 given depth or location. We examined the relative changes in $P_{c\text{ DOC}}$ and $P_{c\text{ }^{14}\text{C}}$ values of our
18 isolated UDOC retentates from the concentration and diafiltration modes in order to explore if
19 changes in DOM molecular size and radiocarbon distributions are apparent with depth. As
20 detailed in the methods, we defined DOC permeation coefficients as “ $P_{c\text{ DOC}}$ ” and $\Delta^{14}\text{C}$
21 permeation model coefficients as “ $P_{c\text{ }^{14}\text{C}}$ ”.

3.4.1 Concentration mode permeation coefficients

In the concentration mode, $P_{c\text{ DOC}}$ values increase with depth from 0.19 to 0.26 – 0.28 (Table 2A, Figure 5A), reflecting overall higher recoveries of HMW DOM for surface vs. deep water (Table 1). These values are consistent with a modeled seawater DOC mixture by Benner et al. (1997) containing 20% HMW ($P_{c\text{ DOC}} = 0$), 50% LMW ($P_{c\text{ DOC}} = 1.0$) and 30% “intermediate” material ($P_{c\text{ DOC}} = 0.5$). A regression of $\ln(C_f/C_0)$ vs. $\ln(CF)$ applied to the solution over $CF = 10,000$ resulted in a $P_c = 0.16$ ($R^2 = 0.98$). The increasing $P_{c\text{ DOC}}$ values with depth determined in this study, could derive from two endmember possibilities: 1) the increase in $P_{c\text{ DOC}}$ reflects only a greater concentration of LMW DOM relative to HMW material at depth, or 2) the ratio of LMW to HMW DOM remains constant with depth, but a significant difference in LMW and/or HMW DOM chemical composition (i.e. molecular size, shape, flexibility, hydrodynamic radius and electrochemical properties) alters rates of HMW rejection and LMW permeation between the surface and deep. However, the latter would require substantial HMW breakthrough during concentration mode, inconsistent with our results and those from previous studies (e.g. Guo et al., 2000). Thus, observed increases in $P_{c\text{ DOC}}$ values at depth (Figure 5A) likely indicate a slightly more heterogeneous distribution of DOM molecular sizes in the surface ocean (i.e. more retainable HMW chemical species) and a more homogeneous molecular size distribution in the deep ocean (far fewer retainable HMW species).

While this interpretation has been inferred by previous studies based solely on HMW recovery, the specificity of P_c values shows the potential for more sensitive (and CF -independent) $P_{c\text{ DOC}}$ values to better quantify the distribution of HMW vs. LMW DOM in different environments. For example, Figure 4 shows that the ranges of P_c values reported for different marine environments are very large. The contrast between observed $P_{c\text{ DOC}}$ values determined in this study from an oligotrophic gyre and those previously reported for the Gulf of

Mexico and Galveston Bay estuary ($\text{TDOC} = 241 - 245 \mu\text{M}$ and $\text{Pc}_{\text{DOC}} = 0.45 - 0.67$ by Guo et al., 2000), may reflect distinctive DOM MW distributions between these distinct marine environments. It should be noted that UF membranes behave differently in solutions of different ionic strength, and therefore caution should be used when comparing Pc values from environments of drastically different salinities (e.g. river vs. seawater). However, changes in UF behavior within seawater salinity ranges are much less likely. In general, decreasing Pc values as a function of increasing solute molecular weight have also been reported in previous studies (Guo et al., 2000; Kilduff and Weber, 1992; Logan and Qing, 1990). While further investigation is needed, it seems likely that relative changes in measured Pc_{DOC} values could serve as proxies for changes in HMW vs. LMW DOM spatial distributions in the ocean.

We also explored a similar approach using modeled $\text{Pc}_{14\text{C}}$ values to approximate the distribution of DOM $\Delta^{14}\text{C}$ -content along depth profiles. In $\Delta^{14}\text{C}$ permeation models, $\text{Pc}_{14\text{C}}$ represents the ratio of LMW ^{14}C -content (permeating the membrane) to HMW ^{14}C -content “retained” by the membrane. As defined by our model (*see methods*), a $\text{Pc}_{14\text{C}} = 1.0$ (slope of zero) would indicate that TDOC is completely homogenous with respect to $\Delta^{14}\text{C}$ -content and that the $\Delta^{14}\text{C}$ value of UDOC is independent of CF (and MW). In other words, a $\text{Pc}_{14\text{C}} = 1.0$ indicates that both LMW and HMW DOC have the same $\Delta^{14}\text{C}$ value. In contrast, large slopes in the model would correspond to very low $\text{Pc}_{14\text{C}}$ values, and would generally signify either a large amount of low- $\Delta^{14}\text{C}$ DOC (older carbon) permeating in the LMW fraction during the concentration mode, the continued retention of $\Delta^{14}\text{C}$ -enriched (modern) HMW compounds during UF, or both. Our model-derived $\text{Pc}_{14\text{C}}$ values are lower in the surface (0.86) and increase in the mesopelagic (~0.98) (Table 2B, Figure 5A). This is consistent with the relatively small offsets between

1 TDOC $\Delta^{14}\text{C}$ and D-UDOC_{HCF} $\Delta^{14}\text{C}$ at depth (~173 ‰ and ~101 ‰, at 670 m and 915 m) vs. in
2 the surface (~240 ‰ at 20 m; Table 1).

3 3.4.2 Diafiltration mode permeation coefficients

4 $P_{c\text{ DOC}}$ and $P_{c\text{ 14C}}$ values were also determined in diafiltration mode (Table 2 A/B, Figure
5 5B; see methods section 2.3). We note that because only the starting concentration of UDOC
6 isolates (UDOC_{HCF}) and the final concentration of UDOC after diafiltration (D-UDOC_{HCF}) were
7 measured ($n = 2$ for each NELHA depth), it is not possible to assess correlation coefficients (R^2)
8 or significance (p -values). However, we believe the trends in these P_c values with depth can still
9 provide meaningful information regarding permeation with MW and $\Delta^{14}\text{C}$ during diafiltration.

10 Estimated $P_{c\text{ DOC}}$ values for diafiltration are similar to $P_{c\text{ DOC}}$ values from the
11 concentration mode (0.16 - 0.13). However, in contrast to concentration mode data, diafiltration
12 $P_{c\text{ DOC}}$ values *decrease* with depth, from $P_{c\text{ DOC}} = 0.16$ in the surface to average $P_{c\text{ DOC}} = 0.13$ in
13 the mesopelagic (Figure 5B). In the surface, the diafiltration $P_{c\text{ DOC}}$ value is also higher relative to
14 that determined for concentration mode (0.16 vs. 0.13), again reflecting the greater relative
15 permeation of LMW DOC during the diafiltration step. In contrast, estimated mesopelagic $P_{c\text{ DOC}}$
16 values are smaller during diafiltration vs. concentration mode (0.13 vs. ~0.27), suggesting that
17 relatively *less* LMW DOC is permeated as a result of changing ionic strength (diafiltration) in
18 deep water. These observations are consistent with mass balance results discussed above,
19 indicating greater permeation of LMW material in surface vs. mesopelagic during diafiltration.

20 Estimated $P_{c\text{ 14C}}$ values during diafiltration also display a clear offset between surface and
21 depth: the estimated surface $P_{c\text{ 14C}}$ value (~0.36) is much higher than mesopelagic $P_{c\text{ 14C}}$ values
22 (~0.12, $n = 2$). Here the relative overall change in UDOC $\Delta^{14}\text{C}$ content is highest in the surface
23 (Table 1: ~93% change in $\Delta^{14}\text{C}$ from UDOC_{HCF} to D-UDOC_{HCF}) and far lower at depth (Table 1:

22% and 17% for 670 m and 915 m, respectively). Thus, these $\text{Pc}_{14\text{C}}$ values are consistent with the large overall change in UDOC $\delta^{14}\text{C}$ content in the surface vs. relatively small change in $\delta^{14}\text{C}$ HMW signatures at depth during diafiltration. In addition, these values are consistent with determined LMW $\delta^{14}\text{C}$ permeation during diafiltration by isotopic mass balance, where LMW material permeating the system at depth was “old” (Table 1: $\delta^{14}\text{C} = -553 \text{ ‰} \pm 35 \text{ ‰}$, $n = 2$) in comparison to the permeation of more ^{14}C -enriched LMW in the surface ($\delta^{14}\text{C} = -206 \text{ ‰}$).

While clearly not conclusive, to the best of our knowledge this exploration represents the first reported Pc values used to describe the permeation of $\delta^{14}\text{C}$ from marine DOM during a UF experiment. Our $\delta^{14}\text{C}$ permeation models for the concentration mode demonstrate universally strong correlations between CF and retentate $\delta^{14}\text{C}$ content. However, given the small range in $\text{Pc}_{14\text{C}}$ values determined here, we cannot unequivocally demonstrate that model-derived $\text{Pc}_{14\text{C}}$ values can be applied in an analogous way to evaluate relationships between both DOC MW and $\delta^{14}\text{C}$. Nevertheless, it seems likely that $\text{Pc}_{14\text{C}}$ values (when placed into the context of HMW recoveries and Pc_{DOC} values) may provide LMW vs. HMW ^{14}C -age information irrespective of the CF employed in a UF experiment, and would be relatively straight forward to determine. Given the dynamic range in reported $\delta^{14}\text{C}$ values across marine environments, it is also possible that significant differences in $\text{Pc}_{14\text{C}}$ values may be potential indicators of DOM ^{14}C -age heterogeneity in different environments.

3.5 Re-evaluation of open ocean HMW DOC $\delta^{14}\text{C}$, reactivity and composition

If UF behaves ideally in terms of $\delta^{14}\text{C}$ permeation and retention, then the basic trends we have identified should be universal and can be extended to other studies. Specifically, similar relationships between CF and $\delta^{14}\text{C}$ would be predicted for UDOM isolated from at least comparable ocean regions. To test this idea, figure 6 summarizes all published surface and

mesopelagic $\delta^{14}\text{C}$ values for HMW DOC vs. corresponding CF data for the Pacific (including results from this study). The predicted effect of increasing CF on the enrichment of HMW DOC $\delta^{14}\text{C}$ -content is clear in both surface and deep water, and is remarkably consistent across all (diafiltered and non-diafiltered) published HMW data. Despite the fact that the compiled data comes from different membrane manufacturers (e.g. Amicon and GE Osmonics) and variable field operation conditions, statistically significant y vs. log x regression correlations are obtained for both surface and mesopelagic data sets ($R^2 = 0.91$, $p = 0.0038$ and $R^2 = 0.81$, $p = 0.0149$, respectively). This comparison seems to confirm that our main conclusions regarding CF and $\delta^{14}\text{C}$ are universal.

Together, these results indicate that when both variable-CF UF and diafiltration are used as key operational parameters, UF can become a highly versatile tool for isolation of the marine DOC pool for composition and $\delta^{14}\text{C}$ studies. In general, using low CFs will effectively retain both HMW and LMW material, resulting in UDOC samples with $\delta^{14}\text{C}$ values nearly representative of TDOC. For example, in the mesopelagic CNP, UDOC at low CFs have $\delta^{14}\text{C}$ signatures very similar to the average TDOC $\delta^{14}\text{C}$, and surface UDOC $\delta^{14}\text{C}$ values are only moderately higher vs. surface TDOC $\delta^{14}\text{C}$ (Figure 6). Subsequent diafiltration will significantly alter $\delta^{14}\text{C}$ values of UDOC collected at any CF. However, while UDOC isolates have traditionally been de-salted; diafiltration is actually not required for many molecular level analyses. For example, both total lipid extraction and acid hydrolysis (to liberate polar biopolymer constituents) can be readily performed in presence of some salt, and further desalting can be accomplished after hydrolysis by resin methods if required (Repeta and Aluwihare, 2006). In contrast, using high CFs coupled with diafiltration allows for the highly selective isolation of the most $\delta^{14}\text{C}$ -enriched DOC components from both surface and mesopelagic waters (Figure 6). In

1 deep waters, HMW DOC is still substantially ^{14}C -depleted ($\Delta^{14}\text{C} \sim -250 \text{ ‰}$) vs. surface sources,
2 however in oligotrophic surface waters HMW DOC is typically fully modern (Figure 6). While it
3 might be tempting to conclude that more extensive diafiltration alone should be an easier way to
4 remove all LMW DOC (and that all diafiltered UDOC samples would thus approach the same
5 $\Delta^{14}\text{C}$ value), figure 6 clearly suggests this is not the case. If diafiltration did remove all LMW
6 material, irrespective of CF, all diafiltered samples in Figure 6 (each with different CFs) should
7 have approximately the same $\Delta^{14}\text{C}$ content. However, they do not, and instead fall on a
8 predictable linear regression with CF representing the principle driving variable. Overall, these
9 results suggest that variable-CF UF experiments can be used as a new tool to target desired
10 portions of the DOC pool, based on relative $\Delta^{14}\text{C}$ value and presumed reactivity, for isolation
11 and study. By coupling molecular-level analyses with variable CF experiments, it is possible we
12 can now gain insight into molecular-level variations within different DOC ^{14}C -age classes.

13 The strong relationship between DOC and $\Delta^{14}\text{C}$ retention during UF also suggests that
14 the chemical composition of a UDOC sample can be influenced by both CF and de-salting. This
15 observation may have important implications for assessing the overall “representativeness” of
16 DOC that can be isolated by this method. UF typically isolates ~15 to 30% of the total DOC
17 pool, and a key question has long been how “representative” such isolates are of the total
18 dissolved material. Most studies have shown that despite relatively modest recoveries of TDOC,
19 UDOC isolates are generally representative of total DOC in terms of their *bulk* composition
20 (Benner et al., 1997; Benner et al., 1992; McCarthy et al., 1993). However, differences have also
21 been reported in terms of both specific molecular-level composition (Dittmar et al., 2001; Skoog
22 and Benner, 1997), and bulk $\Delta^{14}\text{C}$ signatures (Loh et al., 2004; McNichol and Aluwihare, 2007).

1 Our results strongly suggest that CF is a central factor in the outcome of any such comparison,
2 one that to our knowledge has not been explicitly considered.

3 We hypothesize that, as with $\Delta^{14}\text{C}$, the overall chemical composition of UDOC would be
4 very similar to Total DOC at low CF, especially in the subsurface ocean. This view is supported
5 by a growing body of data on both the major biochemical components of ocean DOC, and also
6 how these vary in the surface vs. subsurface ocean. The ^{14}C -depleted material in the subsurface
7 ocean is dominated by aliphatic and carboxyl functions (Benner et al., 1992; McCarthy et al.,
8 1993), now hypothesized to be predominantly composed of a family of carboxyl-rich alicyclic
9 structures (Hertkorn et al., 2006). In contrast, the ^{14}C - modern “semi-labile” material added and
10 remineralized in the upper ocean appears to be quantitatively dominated by HMW oligo- and
11 polysaccharides (Aluwihare et al., 1997; Benner et al., 1992; McCarthy et al., 1996; Pakulski and
12 Benner, 1994).

13 While clearly an important simplification, one can conceptualize major ocean DOC
14 composition as a mixture of these two general components. This basic model is strongly
15 supported by data from a new approach which allows nearly quantitative DOC recovery using
16 electrodialysis/reverse osmosis (Koprivnjak et al., 2009). The overall solid-state NMR spectra of
17 surface DOC isolated by RO-ED (representing up to ~75% of total DOC pool) are very similar to
18 those for UDOC isolates; the only major difference being that additional carboxyl-rich alicyclic
19 material (CRAM) is present in the RO-ED sample (Koprivnjak et al., 2009). Koprivnjak and
20 coauthors averaged literature UDOC NMR spectra for this comparison, combining results from
21 UDOC isolates with variable, but typically high, CF values. Based on our results, we hypothesize
22 that a comparison of RO-ED material with low-CF UDOC should yield nearly identical NMR
23 spectra, certainly for deep water. If proven, this would suggest that CRAM predominantly exists

1 within the LMW DOC pool. In contrast, a comparison of RO-ED isolates with ultra-high CF
2 UDOC (>5,000) would be hypothesized to show even greater compositional divergence. This
3 thought experiment illustrates how variable CF could be used to target desired portions of the
4 DOC pool for study: the most labile, polysaccharide-dominated HMW DOC fraction can be
5 effectively isolated from most CRAM by using very high CFs and diafiltration in surface waters,
6 while TDOC-representative samples of CRAM-enriched deep DOC can be isolated using low-
7 CF experiments.

8

4. Overview and Implications

Our results demonstrate that in UF isolations of oceanic DOC, CF can be used a proxy for MW distribution for a variety of experimental purposes. Even in large-volume experiments with extremely high CFs, oceanic DOC and its associated $\delta^{14}\text{C}$ values still behave ideally in terms of theoretical UF permeation models. However, high CF isolations of oceanic DOC (including during diafiltration) also continued to result in the substantial permeation of LMW DOC - far beyond what might have been expected from lower CF ranges used in some prior studies - leading to large effects in DOC and $\delta^{14}\text{C}$ recovery. As a consequence, changes in both TDOC and $\delta^{14}\text{C}$ are closely linked, and can be explicitly predicted using UF permeation models. Finally, the P_c values produced by these models also may provide a new approach for understanding DOC molecular size and $\delta^{14}\text{C}$ -age distributions in the ocean. Together these observations suggest that in practice the chemical and isotopic composition of a UDOC sample will strongly depend on the CF and diafiltration protocols used. The large range of P_c values for seawater DOC suggests variability in MW distributions between ocean regions. This seemingly precludes the notion of an “optimal” CF, which can be universally applied for the complete removal of LMW DOC (e.g. Guo and Santschi, 1996 and Guo et al., 2000).

The strong relationship between DOC and $\delta^{14}\text{C}$ permeation behavior with UF processing has implications for the study and interpretation of HMW DOC sources and reactivity in the global ocean. Without placing previously reported HMW DOC $\delta^{14}\text{C}$ signatures into the context of CF, the large range in HMW $\delta^{14}\text{C}$ values seemingly indicates large differences HMW DOC reactivity in the upper ocean, even in similar ocean regions. Our results suggest that this is not the case, instead suggesting that semi-labile DOC age and reactivity remain relatively constant in similar ocean regions. These results may also have implications for previously published

1 compound-specific data. Published compound-specific $\delta^{14}\text{C}$ results for oceanic DOC thus far
2 have been derived mostly from high CF, diafiltered UDOC isolates, in some cases using
3 extremely high CFs of $\sim 10,000$ (Aluwihare et al., 2002; Repeta and Aluwihare, 2006). Sugar
4 monomers isolated from such UF samples have modern ^{14}C -ages, however our results suggest
5 these UF conditions should preferentially isolate only the most ^{14}C -modern components. One
6 possibility is that similar experiments conducted with low-CF UDOC (<100) would yield quite
7 different results. However, this would not necessarily be the case, and should in fact depend on
8 the relative distributions of hydrolyzable (and presumably more labile) biochemicals vs. their
9 relative MW in the ocean's DOC pool. This is readily testable, and suggests that the use of
10 variable-CF ultrafiltration, coupled with molecular-level analysis, can offer a new approach to
11 testing fundamental relationships among molecular size, ^{14}C -age, composition and reactivity of
12 oceanic DOC.

5. Table and Figure Captions

Table 1: Summary of NELHA stable isotopic and radiocarbon data.

All $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ data for dissolved organic carbon (DOC) samples are reported in per mil (‰) notation and follow the conventions set forth by Stuiver and Polach (1977). For UDOC_{HCF}, $n = 2$ $\Delta^{14}\text{C}$ analyses were performed; in this case $\Delta^{14}\text{C}$ errors (\pm) represent the range in reported values. Percent recoveries for all UDOC fractions (UDOC_{LCF}, UDOC_{HCF}, D-UDOC_{HCF}) are calculated via determined molar DOC concentrations and total sample volume processed. Volume corrected and retentate DOC concentrations are reported in μM . Low molecular weight (LMW) DOC concentrations are calculated by difference with respect to TDOC, or UDOC sub-fractions, as specified in parenthesis.

Table 2: Summary of permeation model statistics for concentration and diafiltration mode.

Regression coefficients (R^2) values represent correlation coefficients from Model I regression analysis, p represents the p -value for each correlation, m is the slope of the regression line, P_c is the permeation coefficient as described in text (*section 2.3*). † y-intercepts and C_{f0} values derived from $\ln(C_f)$ vs. $\ln(CF)$ regressions (Kilduff and Weber, 1992). All other data are derived from $\ln(C_f/C_{f0})$ vs. $\ln(CF)$ regressions. * Diafiltration mode values were determined using relationships specified in Kilduff and Weber (1992): $\ln(C_f/C_{f0})$ vs. V_p/V_0 because only $n=2$ samples were available, R^2 and p -values were not determined. Measured UDOC-HCF values were used as C_{f0} values in diafiltration mode models.

Figure 1: Summary of isolated DOC fractions.

Cartoon representing sampled UDOC sub-fractions isolated with increasing CF and after diafiltration, in terms of total DOC pool. Measured UDOC sub-fractions include: Total DOC (TDOC) collected at $CF = 1$, UDOC collected at low CF (UDOC_{LCF}; $CF \sim 40$), UDOC collected

at high CF (UDOC_{HCF} ; CF $\sim 3,000$) and UDOC collected after diafiltration from the final 2 L sample retentate ($\text{D-UDOM}_{\text{HCF}}$: top black box). The total column composed of all non/shaded boxes represents the entire DOC pool. White and shaded boxes correspond to DOC progressively lost with increasing concentration factor (CF) and diafiltration, or LMW material lost during the UF process. Recoveries for each fraction are reported as percent of TDOC for determined ranges of surface (20 m) and mesopelagic samples (670 m, 915 m). Figure is not to scale with respect to percent recovery or CF.

Figure 2: UDOC retentate DOC concentration and $\delta^{14}\text{C}$ vs. concentration factor.

A) DOC concentrations in UF retentate sub-samples (μM) at varying concentration factor (CF) and after diafiltration for the three sampled NELHA depths. For all data points, measured errors are smaller than the symbols used. B) Measured retentate DOC $\delta^{14}\text{C}$ values with CF and after diafiltration. Vertical dashed lines in A/B represent change from concentration to diafiltration mode (*see section 2.1, 2.2*).

Figure 3: Permeation models of DOC retention and $\delta^{14}\text{C}$ content during ultrafiltration.

A) DOC permeation model (Kilduff and Weber, 1992). Model I regression lines for each depth are also shown with R^2 values and equations from which permeation coefficients were calculated (*see methods, section 2.3*). B) Radiocarbon permeation model (*see methods, section 2.3*). NELHA depths (20 m, 670 m, and 915 m) are represented by open circles, open triangles, and gray squares, respectively. Vertical dashed lines represent a change in filtration parameters from concentration mode to diafiltration mode (*see methods section 2.3*). All data shown represent the natural log transform of DOC and $\delta^{14}\text{C}$ data reported in Table 1.

Figure 4: Conceptual model of DOC permeation coefficients.

Figure shows permeation coefficient (P_c) theoretical limits (thick lines) and the relationship between P_c and solute mixtures of differing molecular weights. Gray shaded area represents the range of previously reported P_c values for seawater DOC at low concentration factors ($CF < 100$; Guo et al., 2000). Hatched area represents the range in P_c values from surface and mesopelagic depths reported within this study ($P_c = 0.194$ to 0.284). Dashed lines A, B and C represent P_c values of three DOC mixtures containing molecular probes of known MW and P_c (Guo et al., 2000). Line A) Sample feed solution contains an equal mixture (20%) of five molecular probes: Dextran 3kDa ($P_c = 0.03$), Dextran 10kDa ($P_c = 0.0$), Vitamin B12 1.33 kDa ($P_c = 0.15$), Glutathione 0.612 kDa ($P_c = 0.16$) and Rhodamine 0.495 kDa ($P_c = 0.60$), with resulting P_c value for this equal mixture of $P_c = 0.085$. Line B) Sample feed solution contains 1% HMW (Dextran 10 kDa) and 99% LMW (Rhodamine 0.495 kDa), resulting in $P_c = 0.471$. Line C) Sample feed solution contains 100% LMW (Rhodamine 0.495 kDa), resulting in $P_c = 0.600$. All modeled regressions were determined assuming a feed DOC solution of $C_{f0} = 100$ μM .

Figure 5: Model-derived DOC and radiocarbon UF permeation coefficients.

Solid symbols = $P_{c \text{ DOC}}$ values; open symbols $P_{c \text{ }^{14}\text{C}}$ values; circles (20m), triangles (670m) and squares (915m) indicate different sampling depths at NELHA. Panel A) shows concentration mode values. Error bars are extrapolated from the standard error of the regression slope (Table 2); if no error bars are shown, error is smaller than symbol. Panel B) shows diafiltration mode P_c values. As discussed in text (section 3.4.2), because only $n = 2$ analyses were used, no errors were determined.

Figure 6: Summary of published UDOC $\delta^{14}\text{C}$ values and relationship to concentration factor: Central North Pacific Ocean.

Surface (3-20 m) and mesopelagic (600 – 2,000 m) ranges in known NPSG TDOC $\delta^{14}\text{C}$ values (hatched rectangles). TDOC $\delta^{14}\text{C}$ ranges are: surface = -137 ‰ to -246 ‰, deep = -405 ‰ to -533 ‰ (Druffel et al., 1992, Bauer et al., 1992, this study). Solid horizontal bars show average TDOC values from these ranges. With the exception of the low CF samples reported within this study, all other HMW DOC data points represent the $\delta^{14}\text{C}$ content of diafiltered UDOC isolates. Solid triangles represent $\delta^{14}\text{C}$ and CF data reported within this study (n = 1 surface and n = 2 average of 670 m and 915 m samples). Open diamonds, circles and squares represent values reported by Loh et al., 2004, Repeta and Aluwihare, 2006, and Guo et al., 1996, respectively. The +10‰ surface and -258‰ deep values reported by Repeta and Aluwihare, in addition to the -502‰ value reported by Guo et al., 1996, represent samples taken from the same site (NELHA) as this study. Because only 1 or 2 samples are reported for each time/location, y error bars represent the total range in reported $\delta^{14}\text{C}$ values. Similarly, x-error bars represent the total range of either reported CF values (this study) or possible CF values, when general ranges in literature sample volumes were reported in place of specific sample volumes (e.g. Loh et al., 2004; Repeta and Aluwihare et al., 2006).

6. Tables and Figures

Table 1: Summary of NELHA stable isotopic and radiocarbon data.

Sample Fraction	Volume (l)	Concentration Factor	Recovery %TDOC	Vol. Corr. DOC	Retentate DOC	$\delta^{13}\text{C}$ \pm	UC/CAMS ID	$\Delta^{14}\text{C}$ \pm	Fm \pm	^{14}C Age (ybp) \pm	DOC	$\delta^{13}\text{C}$	LMW DOM $\Delta^{14}\text{C}$	^{14}C Age (ybp)
TDOC														
21 m	2.0	1	100	73	73	-20.4	0.2	-246	5	0.7596	0.0018	2,210	5	2,650
670 m	2.0	1	100	40	40	-21.7	0.2	-479	9	0.5249	0.0030	5,180	9	5,430
915 m	2.0	1	100	43	43	-23.2	0.2	-446	8	0.5583	0.0026	4,680	8	4,860
UDOC_{LCF}														
21 m	2,830	28	32	23.4	1,162	-21.2	0.3	-131	3	0.8747	0.0032	1,080	30	2,860
670 m	3,130	46	22	8.9	714	-21.6	0.2	-424	3	0.5797	0.0028	4,380	40	5,480
915 m	3,010	38	22	9.3	351	-22.3	0.2	-552	3	0.4515	0.0028	6,390	60	4,320
UDOC_{HCF}														
21 m (n=2)	5,450	2,725	21	15.1	43,242	-21.5	0.2	-80	1	0.9261	0.0013	620	20	2,030
670 m (n=2)	6,035	3,018	12	4.7	12,414	-21.7	0.1	-393	2	0.6112	0.0018	3,950	25	4,940
915 m (n=2)	4,990	2,495	11	4.8	13,406	-21.7	0.1	-415	2	0.5887	0.0022	4,260	30	9,650
D-UDOC_{HCF}														
21 m	5,450	2,725	13	9.5	22,487	-22.1	0.2	-6	4	1.0008	0.0043	> Modern	-	1,860
670 m	6,035	3,018	7	2.8	8,894	-21.3	0.1	-306	2	0.6986	0.0022	2,880	35	5,870
915 m	4,990	2,495	8	3.4	9,536	-21.4	0.2	-345	2	0.6594	0.0025	3,350	35	7,120

Table 2: Summary of permeation model statistics for concentration and diafiltration mode.

A) DOC Permeation Model Results:

Depth (m)	R ²	p	m	P _{c DOC}	±	y-int [†]	±	C _{10 DOC} [†] (μM)	±
concentration mode									
20	0.9999	0.005	0.807	0.194	0.006	4.31	0.03	74	2
670	0.9994	0.016	0.716	0.284	0.018	3.73	0.09	42	4
915	0.9867	0.074	0.737	0.263	0.086	3.55	0.43	35	15
diafiltration mode*									
20	1.0	-	-0.165	0.165	-	0.0	-	43,242	-
670	1.0	-	-0.133	0.133	-	0.0	-	12,414	-
915	1.0	-	-0.134	0.134	-	0.0	-	13,406	-

B) |DOC Δ¹⁴C| Permeation Model Results:

Depth (m)	R ²	p	m	P _{c 14C}	±	y-int [†]	±	C _{10 14C} [†] (‰)	±
concentration mode									
20	0.9765	0.098	0.140	0.860	0.022	5.45	0.11	-232	25
670	0.9772	0.097	0.025	0.975	0.004	6.16	0.02	-474	9
915	0.0754	0.823	0.010	0.990	0.036	6.19	0.18	-486	88
diafiltration mode*									
20	1.0	-	-0.360	0.360	-	0.0	-	-80	-
670	1.0	-	-0.125	0.125	-	0.0	-	-393	-
915	1.0	-	-0.119	0.119	-	0.0	-	-415	-

Figure 1: Summary of isolated DOC fractions.

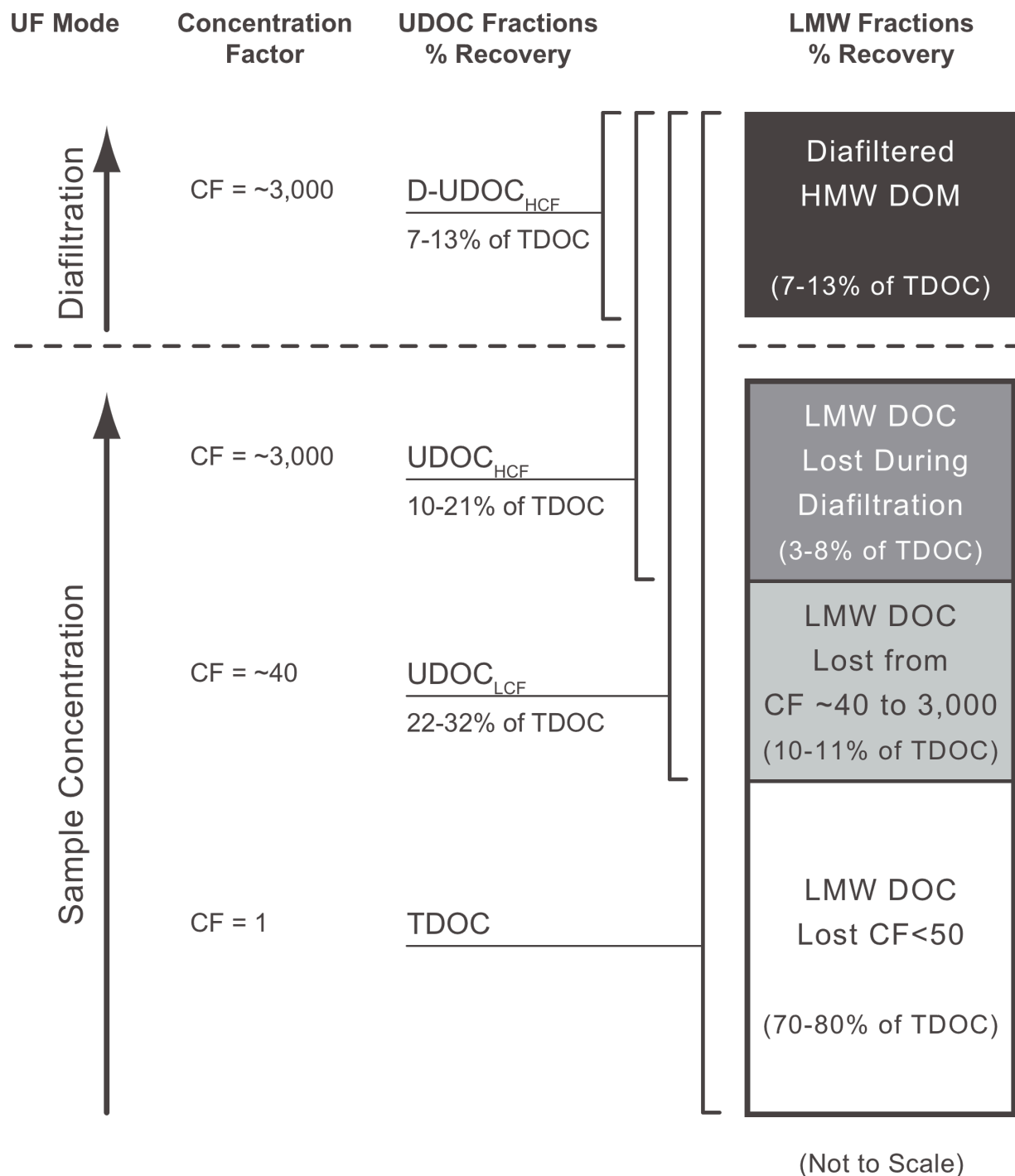


Figure 2: UDOC retentate DOC concentration and $\Delta^{14}\text{C}$ vs. concentration factor.

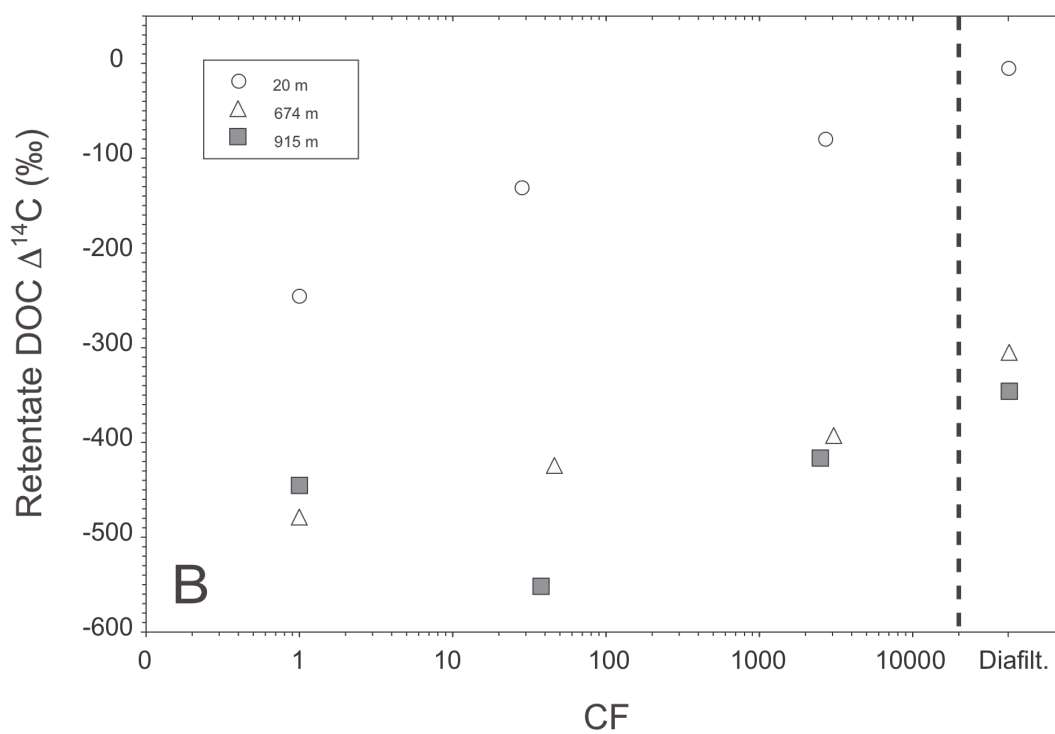
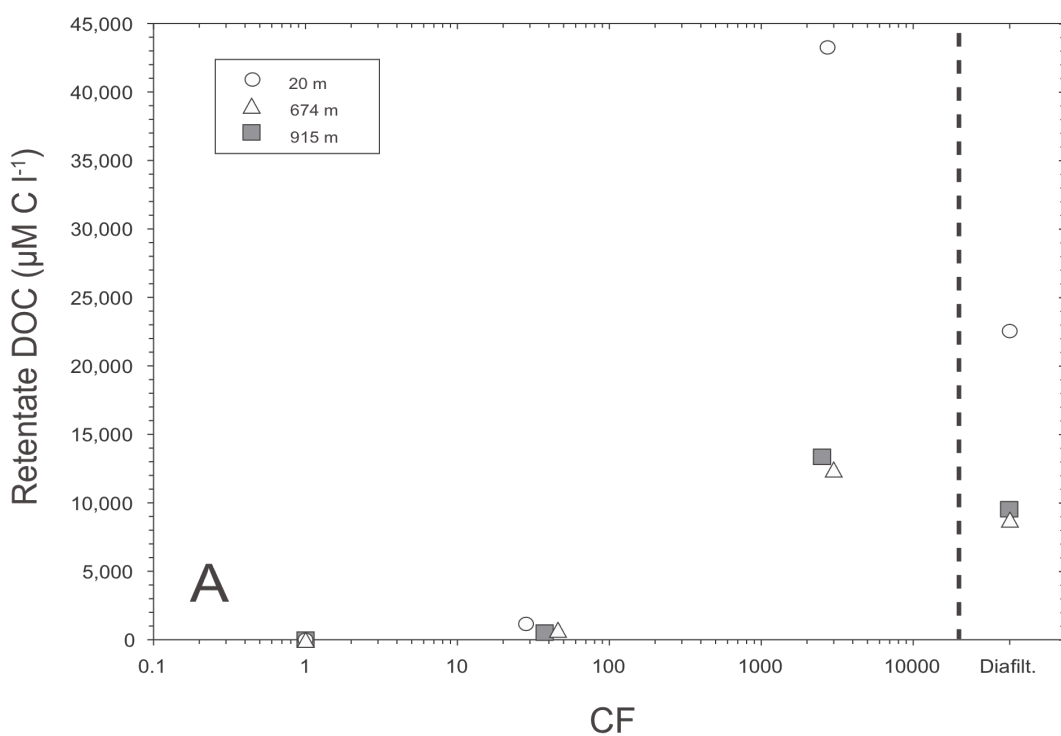
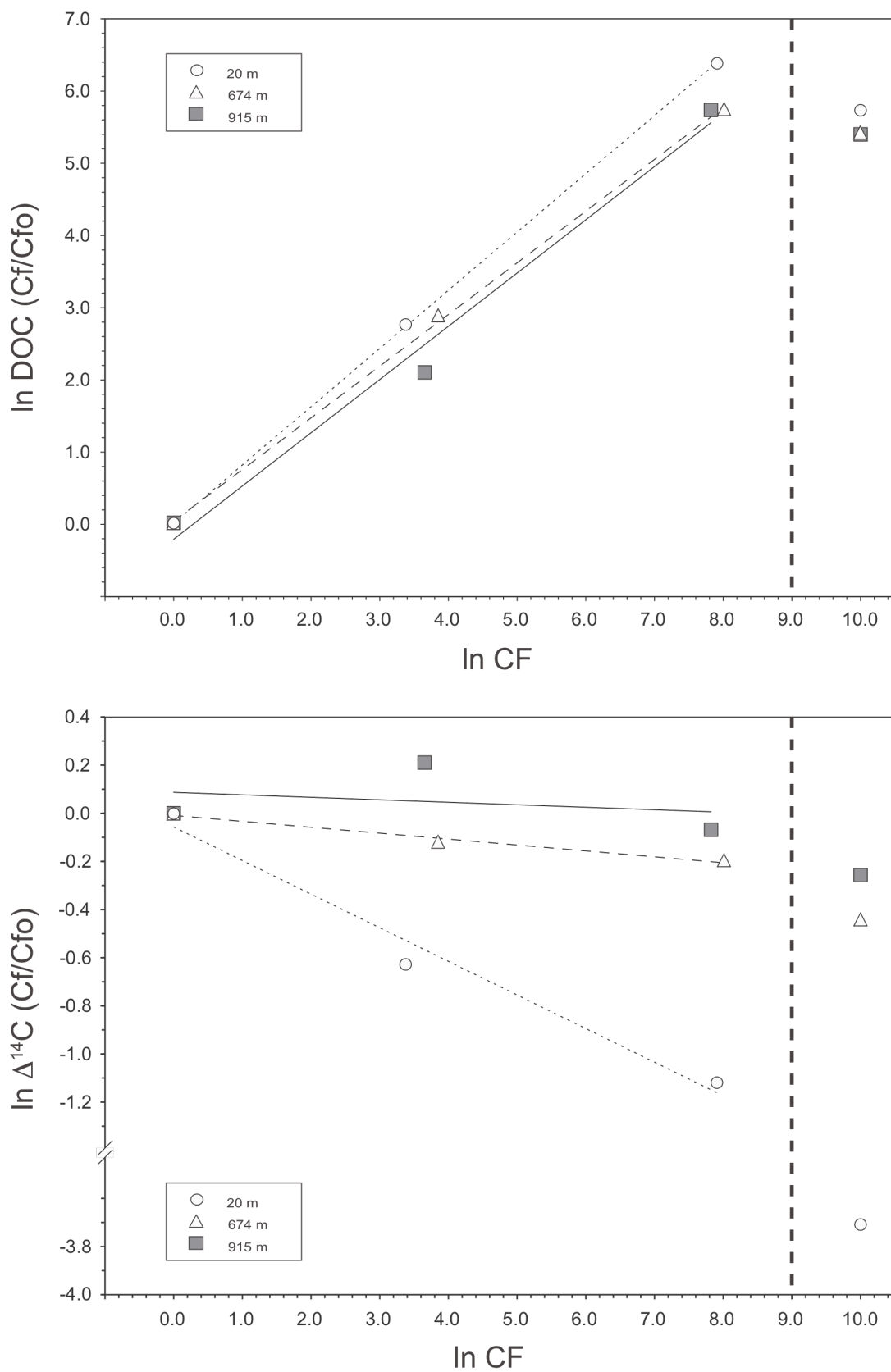


Figure 3: Permeation models of DOC retention and $\delta^{14}\text{C}$ content during ultrafiltration.



1 Figure 4: Conceptual model of DOC permeation coefficients.
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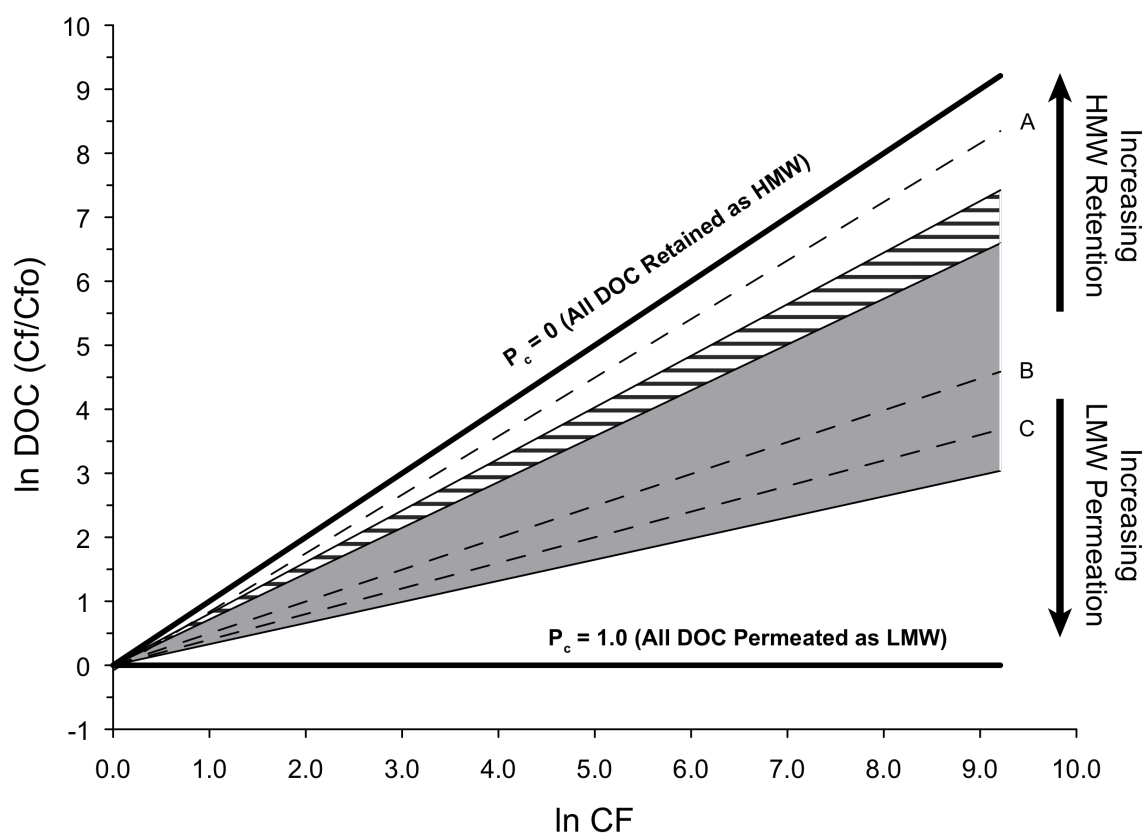


Figure 5: Model-derived DOC and radiocarbon UF permeation coefficients.

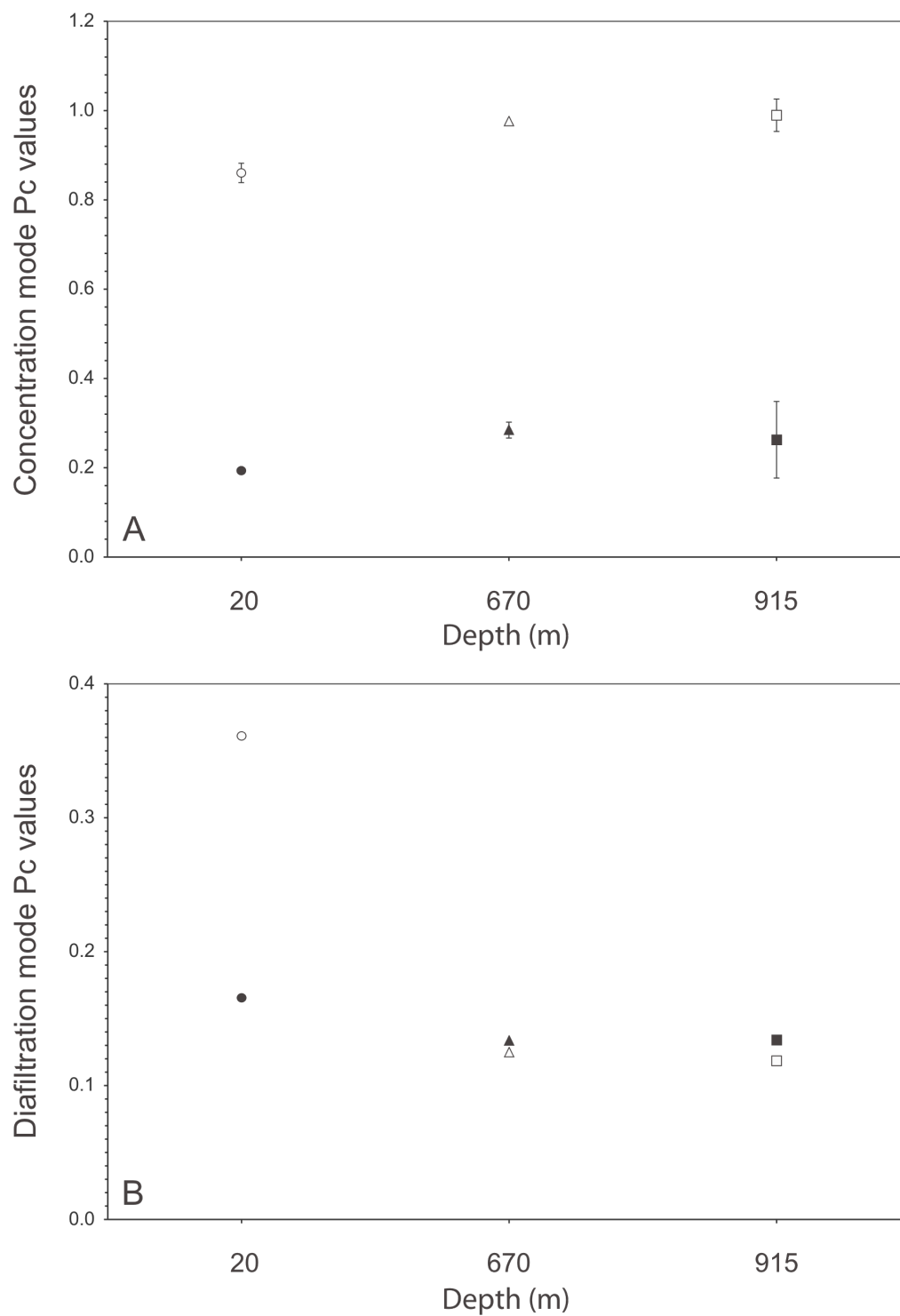
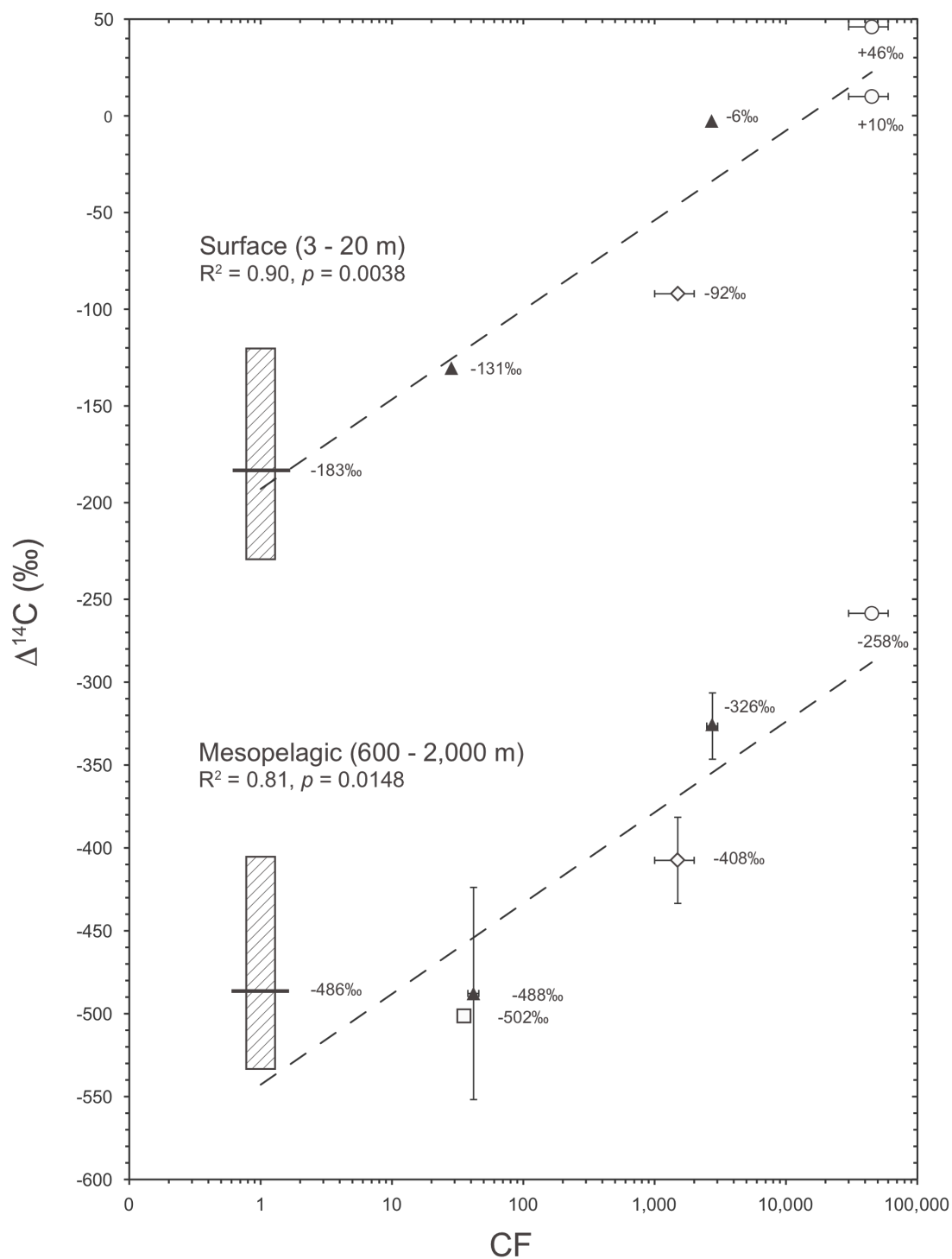


Figure 6: Summary of published UDOC $\Delta^{14}\text{C}$ values and relationship to concentration factor: Central North Pacific Ocean.



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